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Interactive comment on "Evaluation of detailed aromatic mechanisms (MCMv3 and MCMv3.1) against environmental chamber data" *by* C. Bloss et al.

C. Bloss et al.

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We are grateful to both referees for the useful comments which we have addressed as follows :

Anonymous Referee #1 Specific comments (mostly minor) 1. Some of the measurement quality should be discussed a little bit more in order to assess if the discrepancies between model and measurements are really due to defi- ciencies in the model or if they could be attributed to measurement uncertainties.

The uncertainty in measurements has been discussed in more detail by Zador et al (2004) and by Volkamer et al. (2002) Typical values have been added to the text

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in section 3. The relation between LIF measurements and OH calculated from the decrease in the yield of the aromatic has been discussed by Bloss et al. (2003)

2 Page 5688 : Only the measurement methods of ozone, NO and NO2 are mentioned at this point.

More detailed discussion is given in the experimental section.

3. Page 5689 : ozone production is NOx sensitive in southern Europe. This is certainly not true for Milano and for other larger urban plumes (several papers published) and will not be true for the colder seasons in large areas.

The text has been changed to ’can be NOx limited’

4. Page 5691 : The average loss rate could be mentioned.

The range of applied dilution rates was (1.2 - 2) x 10-5 s-1, and this has been added to the text.

5. Probably it is mentioned somewhere, but the humidity could be added in Table 1.

The humidity used in the simulations was that measured throughout the experiment as a function of time. Typical water mixing ratios were 40 - 70 ppm and this has been added to section 2.4.

6. Page 5692: The net ozone production would strictly be the conversion of NO to NO2 by reaction with peroxy radicals minus the chemical losses (O1D + H2O; O3+OH; O3+HO2; O3 + alkenes, ˇ E)

’net’ has been omitted

7. Page 5695: In the p-xylene case, a problem with the UV-ozone instrument is postulated. Why is then not the FTIR-data used for all cases for comparison with the model.

The FTIR measurements were on a much lower time base than the UV data, and points exhibited more scatter. Therefore, where the two measurements were consistent it was considered more appropriate to use the UV measurements for comparison with the model.

8 Page 5695: It could be mentioned how well the LIF OH measurements compared to OH calculated from decays of compounds where OH degradation is the only important pathway. This is also important for the companion paper as OH from LIF measurements are compared to the model.

We have added: These measurements show good agreement between [OH] calculated from the rate of decay of the aromatic and that measured by LIF, confirming the validity of the FAGE calibration within the quoted 1s measurement uncertainty of 26%

9. Page 5697 line 8/9: ‘not completely eliminate the ozone prediction’. In the high NOx case the ozone prediction is still very high.

’completely’ has been omitted.

10. Page 5698: the year of the reference Zador and Pilling should be 2004.

This has been changed.

11. Page 5700: concerning the gloxal discussion : how important might be a pathway to the aerosol phase?

Discussion has been added in section 4.2.4 see point 13 below.

12. Page 5708 line 18: Only MCMv3 is mentioned but not MCMv3.1 for this point.

The details in the paper quoted (Hamilton et al. 2003) relate to MCMv3, but as that paper notes, the same conclusions apply with the modified mechanism MCMv3.1 and this has now been reflected in the text.

13. In the discussion, the new findings on secondary aerosols from aromatics including polymerization reactions could be mentioned. As was shown in the paper of Kalberer et al. (2004), also low molecular weight molecules and rather reactive molecules like

HCHO could be incorporated into the aerosol and might influence also the gas phase reaction scheme even if the total aerosol produced might not seem so high.

Some new text has been added to section 4.2.4 on the potential for ring opened compounds to go into the aerosol.

Anonymous Referee #2 Specific comments which the authors should consider are: 1) Page 5685. While the uncertainties in the OH radical reaction rate constants are stated in Calvert et al. (2002) to be around 20-25%, Kramp and Paulson (1998) concluded that the rate constants for the reactions of OH radicals with a series of organic compounds, including toluene, m-xylene and 1,3,5-trimethylbenzene, are known to within approximately 10%.

While the Kramp and Paulson measurements have clearly been carried out carefully, this is a single experimental determination. It is more appropriate to utilize the recommendations of evaluations of all existing experimental data. In the absence of such an evaluation of all the aromatic species, the Calvert analysis is the most appropriate. We propose to leave the text as it is.

2) Page 5685, 3 lines from bottom. The Atkinson et al.(1992) reference cited dealt with the reactions of OH radicals and NO3 radicals with phenol and the cresols. Possibly the reference that should be cited here is Atkinson et al. (1989) concerning a product study of OH + benzene.

This suggested change has been made.

3) Pages 5686 and 5691.What about losses of chemicals to the chamber walls, which could be important for low volatility product species?

Text has been added to the introduction to acknowledge that loss of chemicals to the chamber walls may impact on chamber experiments. The wall loss of HNO3 is discussed in section 4.1. In the course of the work simulations were carried out to check the possible impact of loss of polar products, particularly cresol isomers, to chamber walls, using typical rates determined by Volkamer (2001). These processes had little effect and were not included in simulations presented in the paper.

4) Page 5688, line 4 from bottom. I assume that cresol should be cresol isomers or o-, m- and p-cresol.

Yes, changed in the text

5) Page 5690, 7 lines from bottom. I assume that the calculated J(NO2) is for clear-sky conditions? This should be noted or clarified.

Yes. Text changed

6) Page 5694, line 3. Were the fans used only during sample introduction or were they on continually during an experiment?

They were on continuously. Text changed.

7) Page 5703. The typical dilution rate (or range of dilution rates) should be given. If, as stated in the text, the majority of the measured decrease in the benzene concentration in Figure 4 was due to dilution,then the dilution rate was close to 8% per hour, a rather high value.

Typical dilution rates have been included in section 2.4, see comment 4 from referee 1 above.

8) As noted in the article, measurement of selected products (and specifically the first-generation products glyoxal, methylglyoxal and phenol/cresol) provides useful additional information for testing MCMv3. However, no yield data or comparisons of predicted vs experimental data are given for the analyses of other ring-opened products (the third group of key species; page 5708). Data for 3-hexene-2,5-dione, formed as a first generation product from the p-xylene reaction, would appear to be useful for mechanism testing, because this compound can be readily analyzed, appears well behaved in chambers, and its loss processes are understood (Calvert et al., 2002; Bethel et al.,

2000; Tuazon and Atkinson, 2003).

This is discussed on p 5708, which refers to detailed measurements by Hamilton et al (2003) that are substantially lower than the modeled values

9) Table 1. Some of the initial HONO concentrations need to be footnoted; that of 55.5 ppb (row 2) should be footnoted “b” and some notation should be given for those in rows 1, 2 and 13 (presumably “d”?).

These footnotes have been added

10) Table 2. Is the process h  NO2 to be viewed as a light-inducted offgassing of NO2 from the chamber walls?

This has been clarified in the table

References :

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Interactive comment on Atmos. Chem. Phys. Discuss., 4, 5683, 2004.

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